Articles

S–H and S–S Oxidative Addition to Low-Valent Vanadium: Synthesis and Structure of Monocyclopentadienyl- and Dicyclopentadienyl–Vanadium Dithiolate Derivatives

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Vanadium compounds exhibiting a variety of structural types are accessible from oxidative addition reactions employing low-valent vanadium reagents such as Cp_2V and $CpV(CO)_4$. The reaction of Cp_2V with 1,3-propanedithiol yields the mononuclear V(IV) species $Cp_2V(SCH_2CH_2CH_2S)$ (**1**). This EPR-active chelate complex crystallizes in the space group $P2_1/n$ with $a = 7.769$ (4) Å, $b = 13.690$ (3) Å, $c = 11.838$ (2) Å, $\beta = 93.78$ (3)°, $V = 1256$ (1) Å^3, and $Z = 4$. Reaction of Cp_2V with 1,2-benzenedithiol yields the V(IV) species $Cp_2V(o\text{-}S_2C_6H_4)$ (**2**). This compound crystallizes in the space group $P2_1/a$ with $a = 12.722$ (5) Å, $b = 15.520$ (3) Å, $c = 13.983$ (3) Å, $\beta = 90.35$ (3)°, $V = 2761$ (2) Å^3, and $Z = 8$. Cyclic voltammetric studies of both of these V(IV) chelate complexes, **1** and **2**, suggest that these species undergo quasi-reversible one-electron oxidations to the related V(V) cations, although attempts to isolated such oxidation products have been unsuccessful. Reaction of Cp_2V with 1,2-ethanedithiol yields a product which was confirmed crystallographically to be the known species $CpV(\mu\text{-}SCH_2CH_2S)_2VCp$ (**3**), in which four sulfur atoms bridge the two V(III) centers. The structurally similar species $CpV(\mu\text{-}o\text{-}SC_6H_4S)_2VCp$ (**4**) is prepared via reaction of $o\text{-}C_6H_4(SH)_2$ with $CpV(CO)_4$. Compound **4** crystallizes in the tetragonal space group $P4/n$ with $a = 17.165$ (13) Å, $c = 7.889$ (5) Å, $V = 2324$ (3) Å^3, and $Z = 4$. Reaction of $m\text{-}(HS)_2C_6H_4$ with Cp_2V affords the V(III) product $Cp_2V(\mu\text{-}m\text{-}SC_6H_4S)VCp_2$ (**5**). This species crystallizes in the space group *Pbcn* with $a = 15.843$ (4) Å, $b = 11.118$ (2) Å, $c = 12.987$ (5) Å, $V = 2288$ (2) Å^3, and $Z = 8$. The macrocyclic compound $Cp_2V(\mu\text{-}SCH_2CH_2CH_2S)_2VCp_2$ (**6**) is accessible via the reaction of the bis(disulfide) $(SCH_2CH_2CH_2S)_2$ with Cp_2V. The results of these studies are presented and discussed. The synthetic utility of such oxidative additions is considered, and the mechanistic implications of the variety of structural types observed are considered.

Introduction

The propensity of sulfur atoms in thiolate derivatives of the early transition metals to bridge two metal centers affords convenient routes to a variety of early–late heterobimetallic (ELHB) complexes.[1-10] We have previously described several ELHB systems containing either pendant chelating or macrocyclic ligands which exhibit reversible redox chemistry. While the chemistry of ELHB systems continues to be of ongoing interest, we are also interested in the development of new early metal thiolate derivatives which may offer similar redox activity. This has prompted our interest in vanadium–thiolate chemistry. Several groups have addressed and continue to address the chemistry of vanadium–thiolate species associated with biological systems,[11] while others have studied organometallic sulfur systems;[12] however, few have studied the related organometallic V–thiolate chemistry. Thus, we initiated an examination of the reaction chemistry of low-valent vanadium cyclopentadienyl species with dithiolates and disulfides. The results of the present study reflect the accessibility of several stable oxidation states of V, and thus, several structural types of dithiolate derivatives are documented. The synthetic utility of such oxidative additions is considered, and the mechanistic implications of the variety of structural types observed are considered.

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2, employing a Vacuum Atmospheres inert-atmosphere glovebox. Solvents were reagent grade, distilled from the appropriate drying agents under N_2 and degassed by the freeze–thaw method at least three times prior to use. EPR spectra were recorded using a Varian E-12 EPR spectrometer employing DPPH as the external reference. ^1H NMR spectra were recorded on a Bruker AC-300 spectrometer operating at 300 MHz and using trace amounts of protonated solvents as a reference. Cyclic voltammetric experiments were performed employing a BAS-CV27 electrochemical unit using a Pt electrode, a Ag/AgCl reference electrode, and NBu_4BF_4 as the supporting electrolyte in THF. Combustion analyses were performed by Galbraith Laboratories Inc., Knoxville, TN, and Schwarzkopf Laboratories, Woodside, NY. Cp_2V was purchased from Strem Chemical Co., 1,2-ethanedithiol, 1,3-propanedithiol, and 1,3-

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Table I. Crystallographic Parameters

	1	2	4	5
formula	$C_{13}H_{16}S_2V$	$C_{16}H_{14}S_2V$	$C_{22}H_{18}S_4V_2 \cdot 0.5C_6H_6$	$C_{26}H_{24}S_2V_2$
cryst syst	monoclinic	monoclinic	tetragonal	orthorhombic
space group	$P2_1/n$ (No. 14)	$P2_1/a$ (No. 14)	$P4_1/n$ (No. 85)	$Pbcn$ (No. 60)
a (Å)	7.769 (4)	12.722 (5)	17.165 (13)	15.843 (4)
b (Å)	13.690 (3)	15.520 (3)		11.118 (2)
c (Å)	11.838 (2)	13.983 (3)	7.889 (5)	12.987 (5)
β (deg)	93.78 (3)	90.35 (3)		
V (Å^3)	1256 (1)	2761 (2)	2324 (3)	2288 (2)
Z	4	8	4	8
abs coeff, μ (cm^{-1})	10.532	9.675	11.356	9.769
T (°C)	24	24	24	24
R^a (%)	3.21	7.79	4.02	7.90
$R_w{}^b$ (%)	3.70	7.77	4.41	8.21

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w/|F_o|^2]^{1/2}$.

benzenedithiol were purchased from Aldrich Chemical Co., and $(SCH_2CH_2CH_2S)_2$ was prepared by the literature method.[10,13]

Synthesis of $Cp_2V(SCH_2CH_2CH_2S)$ (1), $Cp_2V(o\text{-}S_2C_6H_4)$ (2), $CpV(\mu\text{-}SCH_2CH_2S)_2VCp$ (3), and $Cp_2V(\mu\text{-}m\text{-}SC_6H_4S)VCp_2$ (5). These products were prepared and isolated in much the same manner, and thus only one such preparation is described in detail. Cp_2V (0.050 g, 0.276 mmol) is dissolved in 3 mL of THF. Propanedithiol (0.100 g, 0.926 mmol) is added slowly with stirring. The solution slowly becomes green-black. The mixture is allowed to stand overnight and then filtered. Hexane (1–2 mL) is added. This affords black crystals of **1**. The crystals are isolated by decantation of the mother liquor. **1**: yield 70%; EPR (THF, 298 K) $g = 1.997$, $\langle a_{51V} \rangle = 55$ G. Anal. Calc: C, 54.43; 5.61. Found: C, 54.40; H, 5.60. **2**: yield 65%; EPR (THF, 298 K) $g = 1.998$, $\langle a_{51V} \rangle = 45$ G. Anal. Calc: C, 59.80; H, 4.39. Found: C, 59.60; H, 4.10. **3**: The formulation of the crystalline product **3** was unambiguously confirmed by determination of the crystallographic unit cell parameters and comparison to those published for **3**.[14] **5**: yield 55%. Anal. Calc: C, 62.15; H, 4.81. Found: C, 62.20; H, 4.80.

Synthesis of $CpV(\mu\text{-}o\text{-}SC_6H_4S)_2VCp$ (4). $CpV(CO)_4$ (0.050 g, 0.219 mmol) is dissolved in 3 mL of THF. $o\text{-}C_6H_4(SH)_2$ (0.031 g, 0.219 mmol) is added slowly with stirring. The solution slowly becomes black. The mixture is allowed to stand overnight and then filtered. On standing, black crystalline material **4** is deposited. The product is isolated by decantation of the mother liquor: yield 50%. Anal. Calc: C, 52.56; H, 3.54. Found: C, 52.20; H, 3.50.

Synthesis of $Cp_2V(\mu\text{-}SCH_2CH_2CH_2S)_2)_2VCp_2$ (6). Cp_2V (0.050 g, 0.276 mmol) is dissolved in 3 mL of THF. $(SCH_2CH_2CH_2S)_2$ (0.029 g, 0.138 mmol) is added slowly with stirring. The solution slowly becomes black. The mixture is allowed to stand overnight and then filtered. On standing, black crystalline material **6** is deposited. The product is isolated by decantation of the mother liquor: yield 45%; EPR (THF, 298 K) $g = 1.999$, $\langle a_{51V} \rangle = 52$ G. Anal. Calc: C, 54.43; H, 5.61. Found: C, 54.00; H, 5.50.

X-ray Data Collection and Reduction. X-ray-quality crystals of **1–5** were obtained directly from the preparations as described above. The crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O_2-free environment for each crystal. Diffraction experiments were performed on a Rigaku AFC6-S four-circle diffractometer with graphite-monochromatized Mo Kα radiation. The initial orientation matrices were obtained from 20 reflections located by an autosearch routine. These data were used to determine the crystal system. An automated check of the Laue symmetry confirmed the crystal systems. Ultimately, 25 reflections ($15° < 2\theta < 35°$) were used to obtain the final lattice parameters and the orientation matrix. Machine parameters, crystal data, and data collection parameters are summarized in Table I. The observed extinctions and subsequent refinements confirmed the respective space groups. The data sets were collected in four shells ($4.5° < 2\theta < 50.0°$), and three standard reflections were recorded every 150 reflections. The intensities of the standards showed no statistically significant change over the duration of the data collections. The data were processed using the TEXSAN software program package on a VAX workstation 3520 located in the Department of Chemistry and Biochemistry at the University of Windsor. The reflections with $F_o{}^2 > 3\sigma(F_o{}^2)$ were used in each of the refinements.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[15,16] The heavy-atom positions for each structure were determined using direct methods employing the Mithril option of the TEXSAN package. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix, least-squares techniques on F, minimizing the function $w(|F_o| - |F_c|)^2$ where the weight, w, is defined as $1/\sigma^2(F_o)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of refinement, all the non-hydrogen atoms in **1** were refined as individual anisotropic atoms. For **2**, **3**, and **5**, only the V and S atoms and some of the carbon atoms were refined anisotropically. This was done to maintain a reasonable data:variable ratio. The remaining non-hydrogen atoms were refined isotropically. In all cases, hydrogen atom positions were calculated by assuming a C–H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. In all cases, the hydrogen atom contributions were calculated but not refined. The final refinement data are given in Table I. The largest peaks in the final difference Fourier map calculations showed residual electron densities of no chemical significance. The following data are tabulated: positional parameters (Table II) and selected bond distances and angles (Table III). Thermal parameters and hydrogen atom parameters have been deposited as supplementary material.

Results

The synthetic routes employing vanadocene are summarized in Figure 1. Electrochemical data for **1** and **2** are reported and the cyclic voltammogram of **1** is shown in Figure 2. X-ray crystallographic results for compounds **1**, **2**, **4**, and **5** are illustrated in Figures 3–6, respectively.

Discussion

Syntheses. A number of groups have studied reactions which effect oxidation of vanadocene[17] and decamethylvanadocene[18] with a variety of organic substrates. However, to our knowledge, oxidative additions of S–H to V have received only limited attention.[19] The reaction of vanadocene with 1,3-propanedithiol proceeds to give a green-black solution. The evolution of a gas, presumably H_2, during this time is apparent. Monitoring the reaction as well as the isolated crystalline solid by EPR reveals that the product **1** is a paramagnetic d^1 V(IV) species. The EPR spectrum shows a typical eight-line resonance at $g = 1.997$ with a ^{51}V ($I = {}^7/_2$) hyperfine coupling constant of 55 G. In a similar fashion 1,2-benzenedithiol undergoes oxidative addition to Cp_2V, affording **2**, which also shows an eight-line resonance at $g = 1.998$ with a ^{51}V ($I = {}^7/_2$) hyperfine coupling constant of 45 G. The spectral parameters for **1** and **2** are comparable to those of $Cp_2V(SMe)_2$.[3] These spectral data, as well as analytical data, suggest the empirical formulations for **1** and **2** as $Cp_2V(SCH_2CH_2CH_2S)$ and $Cp_2V(S_2C_6H_4)$, respectively. In related Ti and Zr systems, we have previously found that the solubility of dimeric species of the form $Cp_2M(\mu\text{-}SCH_2CH_2CH_2S)_2MCp_2$ is dramatically less than that of the analogous mononuclear metallocenedithiolates. This suggests that the present V compounds are mononuclear.[8-10] This has been confirmed crystallographically (vide infra).

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(14) Compound **3** crystallizes in the space group $P2_1/c$ with $a = 13.034$ (4) Å, $b = 7.645$ (2) Å, $c = 17.388$ (4) Å, $\beta = 105.00$ (2)°, $V = 1673.5$ (7) Å^3, and $Z = 4$. Structural solution and refinement confirmed the formulation as the known species $CpV(\mu\text{-}SCH_2CH_2S)_2VCp$.[20]

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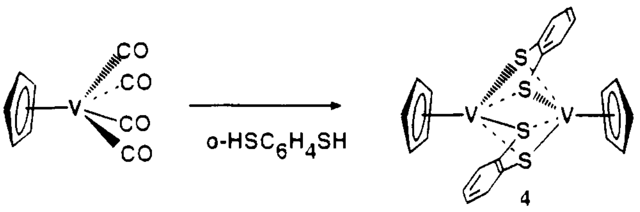
Table II. Positional Parameters

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Molecule 1							
V1	0.36646 (7)	0.15270 (4)	0.68198 (5)	C6	0.4227 (6)	0.0098 (3)	0.7799 (5)
S1	0.4198 (1)	0.31480 (7)	0.75876 (8)	C7	0.5049 (8)	0.0056 (4)	0.6797 (5)
S2	0.4735 (1)	0.21356 (7)	0.50698 (8)	C8	0.6322 (6)	0.0754 (4)	0.6852 (5)
C1	0.0964 (5)	0.1081 (3)	0.7357 (3)	C9	0.6264 (5)	0.1241 (3)	0.7847 (5)
C2	0.0959 (4)	0.2083 (3)	0.7195 (3)	C10	0.4967 (6)	0.0852 (3)	0.8441 (3)
C3	0.1219 (4)	0.2261 (3)	0.6054 (4)	C11	0.6285 (5)	0.3628 (3)	0.7253 (3)
C4	0.1355 (5)	0.1356 (3)	0.5506 (3)	C12	0.6568 (5)	0.3749 (3)	0.6005 (4)
C5	0.1203 (5)	0.0625 (3)	0.6316 (4)	C13	0.6729 (5)	0.2802 (3)	0.5365 (3)
Molecule 2							
V1	0.3690 (2)	0.0395 (2)	0.2535 (2)	C22	0.259 (2)	–0.001 (1)	0.376 (1)
V2	1.1159 (2)	–0.0046 (2)	0.7566 (2)	C23	0.360 (2)	–0.009 (1)	0.411 (1)
S1	0.5078 (3)	0.1449 (3)	0.2282 (4)	C24	0.401 (2)	0.074 (1)	0.409 (2)
S2	0.2765 (3)	0.1433 (3)	0.1541 (4)	C25	0.328 (2)	0.130 (1)	0.377 (1)
S3	0.9988 (4)	0.1059 (3)	0.6939 (4)	C31	0.360 (2)	–0.107 (1)	0.226 (1)
S4	1.2322 (4)	0.1193 (3)	0.7624 (4)	C32	0.466 (2)	–0.084 (1)	0.231 (2)
C1	0.482 (1)	0.176 (1)	0.114 (1)	C33	0.486 (2)	–0.035 (1)	0.156 (2)
C2	0.379 (1)	0.177 (1)	0.077 (1)	C34	0.398 (2)	–0.021 (1)	0.106 (1)
C3	0.354 (1)	0.207 (1)	–0.014 (1)	C35	0.315 (2)	–0.063 (1)	0.147 (2)
C4	0.435 (2)	0.235 (1)	–0.073 (1)	C41	1.095 (1)	–0.130 (1)	0.669 (1)
C5	0.540 (2)	0.235 (1)	–0.039 (2)	C42	1.079 (2)	–0.066 (1)	0.607 (1)
C6	0.562 (2)	0.205 (1)	0.052 (1)	C43	1.174 (1)	–0.018 (1)	0.600 (1)
C7	1.089 (1)	0.171 (1)	0.629 (1)	C44	1.244 (1)	–0.062 (1)	0.660 (1)
C8	1.193 (1)	0.176 (1)	0.662 (1)	C45	1.202 (1)	–0.127 (1)	0.704 (1)
C9	1.259 (1)	0.230 (1)	0.613 (1)	C51	1.065 (2)	–0.098 (1)	0.874 (2)
C10	1.229 (2)	0.277 (1)	0.535 (1)	C52	1.155 (2)	–0.060 (2)	0.906 (2)
C11	1.127 (2)	0.268 (1)	0.502 (1)	C53	1.136 (2)	0.021 (1)	0.919 (1)
C12	1.059 (1)	0.216 (1)	0.550 (1)	C54	1.035 (2)	0.041 (1)	0.894 (1)
C21	0.241 (2)	0.087 (1)	0.353 (1)	C55	0.989 (2)	–0.034 (1)	0.866 (1)
Molecule 4							
V1	0.43749 (5)	0.03244 (5)	0.9550 (1)	C6	0.5321 (3)	0.1204 (3)	1.2789 (7)
S1	0.43925 (8)	–0.10271 (8)	1.0565 (2)	C11	0.3528 (3)	0.0582 (4)	0.7376 (8)
S2	0.47824 (8)	0.03385 (8)	1.2514 (2)	C12	0.3730 (3)	0.1297 (3)	0.8125 (9)
C1	0.4302 (3)	–0.1521 (3)	0.8601 (7)	C13	0.3464 (3)	0.1291 (3)	0.9813 (8)
C2	0.3844 (4)	–0.2183 (3)	0.8414 (9)	C14	0.3108 (3)	0.0571 (3)	1.0094 (8)
C3	0.3779 (4)	–0.2536 (4)	0.685 (1)	C15	0.3138 (3)	0.0139 (3)	0.8595 (9)
C4	0.4154 (4)	–0.2239 (4)	0.548 (1)	C8	0.2010 (8)	0.1848 (7)	0.403 (1)
C5	0.4599 (4)	–0.1563 (4)	0.5624 (8)	C7	0.2611 (9)	0.1699 (6)	0.404 (1)
Molecule 5							
V1	0.1563 (2)	0.1412 (2)	0.0238 (2)	C13	0	0.451 (2)	$-^1/_4$
S1	0.1553 (3)	0.1850 (5)	–0.1592 (3)	C12	0.066 (1)	0.390 (1)	–0.208 (1)
C1	0.077 (1)	0.309 (2)	0.055 (1)	C14	0	0.205 (2)	$-^1/_4$
C2	0.023 (1)	0.215 (1)	0.026 (1)	C6	0.285 (1)	0.074 (2)	–0.033 (1)
C3	0.027 (1)	0.123 (1)	0.097 (1)	C7	0.231 (1)	–0.024 (2)	–0.027 (1)
C4	0.085 (1)	0.159 (1)	0.173 (1)	C8	0.211 (1)	–0.035 (2)	0.078 (2)
C5	0.114 (1)	0.272 (2)	0.146 (1)	C9	0.254 (1)	0.052 (2)	0.126 (1)
C11	0.0674 (9)	0.266 (1)	–0.207 (1)	C10	0.298 (1)	0.123 (2)	0.059 (1)

In the analogous reaction of ethanedithiol and Cp$_2$V, the solution also becomes black and black crystals precipitate. This product **3** is only very slightly soluble in benzene, and it also exhibits no EPR spectrum at 298 K. Subsequent crystallographic examination of **3**[14] showed that it is the known species CpV(μ-SCH$_2$CH$_2$S)$_2$VCp.[20] The structure of **3** is depicted in Figure 1. The related complex CpV(μ-*o*-SC$_6$H$_4$S)$_2$VCp (**4**) was prepared by employing a synthetic route similar to that used for the original preparation of **3**. Thus, oxidative addition of *o*-benzenedithiol to CpV(CO)$_4$ yielded the crystalline product **4**.



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The reaction of Cp$_2$V with 1,3-benzenedithiol proceeds to give a black crystalline product, **5**. In this case however, neither the solution nor the isolated product exhibits an EPR signal at 298 K. The product **5** is soluble in benzene, THF, and hydrocarbons. Nonetheless, the analytical data suggest the formulation of one dithiol to two vanadocene units. Crystals of this product were obtained directly from the reaction mixture, and the formulation of **5** as the V(III) species Cp$_2$V(μ-*m*-SC$_6$H$_4$S)VCp$_2$ was confirmed crystallographically (vide infra).

Reactions of vanadocene with X$_2$, where X is halide or an easily reduced substrate, are well-known to proceed with oxidative addition to V(IV). In the case of disulfides, this too has been employed for the synthesis of complexes of the form Cp$_2$V(SR)$_2$.[17] In an analogous manner, Cp$_2$V was reacted with (SCH$_2$CH$_2$CH$_2$S)$_2$. The reaction proceeds to give a green-black solution and a black precipitate. The EPR spectrum of this product **6** shows an eight-line resonance at $g = 1.999$ with hyperfine coupling to ^{51}V of 52 G. These parameters are very close to those of **1**, suggesting a similar formulation. Again, in related Ti and Zr systems we have shown that the dimeric species Cp$_2$M(μ-SCH$_2$CH$_2$CH$_2$S)$_2$MCp$_2$ can be prepared from the reaction of Cp$_2$Zr and Cp$_2$Ti, generated in situ, and (SCH$_2$CH$_2$CH$_2$S)$_2$.[8–10] In these cases, the formulation has been unambiguously confirmed crystallographically. In addition to this precedent, analytical data and the relatively poor solubility of **6** compared to **1** suggest that **6** is formulated as the bimetallic, macrocyclic species Cp$_2$V(μ-

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(20) Rajan, O. A.; Noordik, J.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics* **1984**, *3*, 831.

Table III. Selected Bond Distances (Å) and Angles (deg)

Molecule 1			
Distances			
V1–S1	2.424 (1)	V1–S2	2.430 (1)
V1–C1	2.314 (4)	V1–C2	2.307 (4)
V1–C3	2.284 (4)	V1–C4	2.308 (4)
V1–C5	2.321 (4)	V1–C6	2.301 (4)
V1–C7	2.284 (4)	V1–C8	2.318 (4)
V1–C9	2.322 (4)	V1–C10	2.303 (4)
S2–C13	1.811 (4)	C11–C12	1.517 (6)
S1–C11	1.817 (4)	C12–C13	1.511 (6)
Angles			
S1–V1–S2	86.91 (4)	S1–C11–C12	116.1 (3)
C11–C12–C13	114.6 (4)	S2–C13–C12	115.5 (3)
V1–S1–C11	112.5 (1)	V1–S2–C13	110.1 (1)
Molecule 2			
Distances			
V1–S1	2.435 (6)	V1–S2	2.426 (6)
V2–S3	2.432 (6)	V2–S4	2.427 (5)
S1–C1	1.70 (2)	S2–C2	1.77 (2)
S3–C7	1.79 (2)	S4–C8	1.72 (2)
V1–C21	2.27 (2)	V1–C22	2.31 (2)
V1–C23	2.33 (2)	V1–C24	2.28 (2)
V1–C25	2.29 (2)	V1–C31	2.31 (2)
V1–C32	2.30 (2)	V1–C33	2.33 (2)
V1–C34	2.29 (2)	V1–C35	2.28 (2)
V2–C41	2.32 (2)	V2–C42	2.34 (2)
V2–C43	2.33 (2)	V2–C44	2.30 (2)
V2–C45	2.32 (2)	V2–C51	2.28 (2)
V2–C52	2.31 (2)	V2–C53	2.32 (2)
V2–C54	2.29 (2)	V2–C55	2.27 (2)
Angles			
S1–V1–S2	79.7 (2)	S3–V2–S4	79.9 (2)
V1–S1–C1	101.0 (6)	V1–S2–C2	100.9 (6)
V2–S3–C7	100.9 (6)	V2–S4–C8	101.6 (6)
Molecule 4			
Distances			
V1–V1	2.520 (2)	V1–S1	2.455 (2)
V1–S1	2.437 (2)	V1–S2	2.441 (2)
V1–S2	2.457 (2)	V1–C11	2.292 (6)
V1–C12	2.298 (6)	V1–C13	2.289 (6)
V1–C14	2.257 (6)	V1–C15	2.275 (6)
S1–C1	1.773 (6)	S2–C6	1.764 (6)
Angles			
S1–V1–S1	117.99 (5)	S1–V1–S2	72.13 (6)
S1–V1–S2	76.79 (6)	V1–S1–V1	62.01 (5)
V1–S1–C1	99.5 (2)	V1–S1–C1	106.2 (2)
V1–S2–V1	61.92 (6)	V1–S2–C6	106.0 (2)
V1–S2–C6	99.4 (2)	S1–C1–C2	122.2 (5)
Molecule 5			
Distances			
V1–S1	2.426 (5)	V1–C1	2.29 (2)
V1–C2	2.26 (2)	V1–C3	2.27 (1)
V1–C4	2.25 (2)	V1–C5	2.26 (2)
V1–C6	2.30 (2)	V1–C7	2.28 (2)
V1–C8	2.25 (2)	V1–C9	2.27 (2)
V1–C10	2.29 (2)	S1–C11	1.77 (1)
Angle			
V1–S1–C11	116.9 (5)		

$SCH_2CH_2CH_2S)_2VCp_2$ (Figure 1). This is also the intuitively expected product, as one might expect the macrocyclic nature of the bis(disulfide) precursor to act as a template for the reaction.

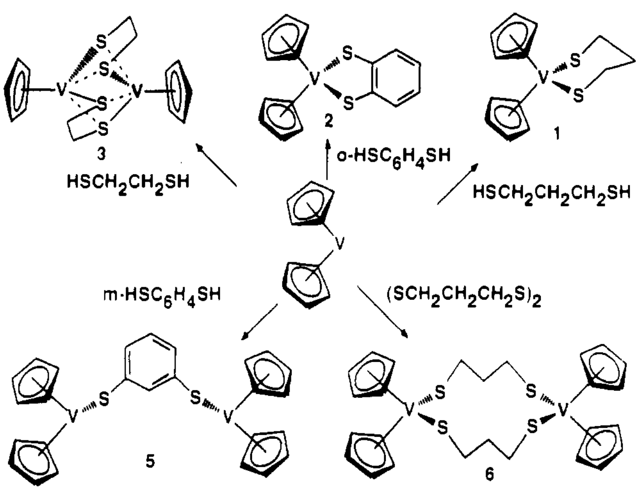


Figure 1. Reactions of vanadocene with dithiols.

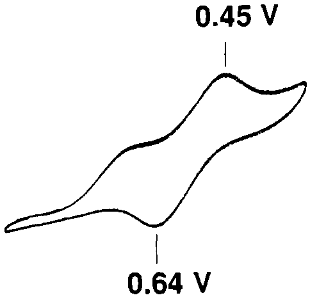


Figure 2. Cyclic voltammogram of $Cp_2V(SCH_2CH_2CH_2S)$ (**1**) recorded in THF (Bu_4NPF_6 supporting electrolyte, Pt working electrode). Potentials are reported relative to the Ag/AgCl reference electrode. The scan rate was 200 mV/s.

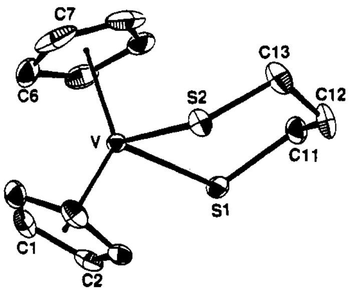
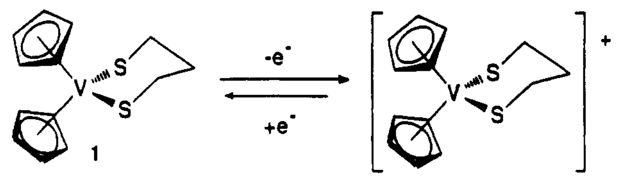


Figure 3. ORTEP drawing of molecule $Cp_2V(SCH_2CH_2CH_2S)$ (**1**). 30% thermal ellipsoids are shown, and hydrogen atoms, which are numbered according to the number of the carbon to which they are bonded, are omitted for clarity.

Electrochemical Studies. Cyclic voltammetric studies of **1** and **2** revealed that both compounds undergo an irreversible reduction at 0.8 and 0.9 V versus Ag/AgCl, respectively. Both species also exhibit oxidation waves. In the case of **1**, this wave was quasi-reversible, being centered at 0.55 V versus Ag/AgCl with a peak-to-peak separation of 190 mV (Figure 2). Compound **2** showed a similar wave, centered at 0.45 V with a peak-to-peak separation of 270 mV. The potentials and peak-to-peak separations are consistent with V(IV)/V(V) couples, as illustrated for **1**:



The quasi-reversible nature of these oxidations may arise from a significant alteration of the geometry at V upon oxidation. Attempts to isolate chemically oxidized **1** and **2** by reaction with Ag(I) salts have been unsuccessful to date, leading only to decomposition. This is in contrast to the case of **3**, which has been shown by Rajan et al.[20] to undergo a facile one-electron oxidation. Electrochemical studies of **5** and **6** are precluded by the poor solubility.

Structural Studies. ORTEP drawings of **1**, **2**, **4**, and **5** are shown in Figures 3–6, respectively. In the case of **1** and **2**, two

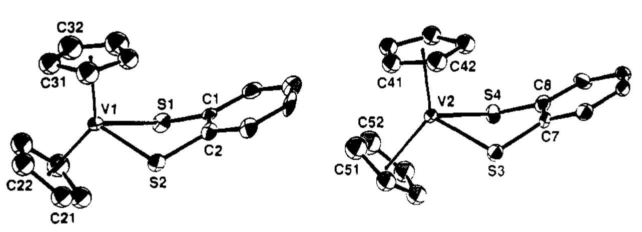


Figure 4. ORTEP drawing of the two independent molecules of $Cp_2V(o\text{-}S_2C_6H_4)$ (**2**) in the asymmetric unit. 30% thermal ellipsoids are shown, and hydrogen atoms, which are numbered according to the number of the carbon to which they are bonded, are omitted for clarity.

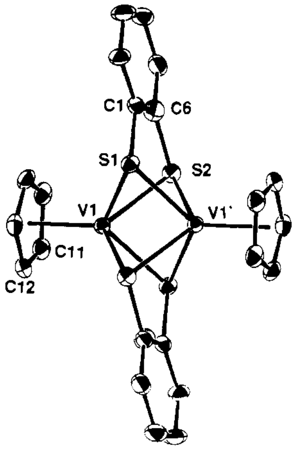


Figure 5. ORTEP drawing of molecule $CpV(\mu\text{-}o\text{-}SC_6H_4S)_2VCp$ (**4**). 30% thermal ellipsoids are shown, and hydrogen atoms, which are numbered according to the number of the carbon to which they are bonded, are omitted for clarity.

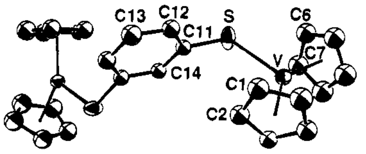


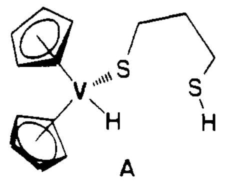
Figure 6. ORTEP drawing of the molecule $Cp_2V(\mu\text{-}m\text{-}SC_6H_4S)VCp_2$ (**5**). 30% thermal ellipsoids are shown, and hydrogen atoms, which are numbered according to the number of the carbon to which they are bonded, are omitted for clarity.

π-bonded cyclopentadienyl rings and two sulfur atoms complete the pseudotetrahedral coordination sphere of vanadium. In **1**, the chelate ring on vanadium adopts a chair conformation, while, in **2**, the planes of the phenyl rings are inclined at angles of 38.3 (1) and 38.4 (1)° relative to the VS_2 planes. The S–C and C–C bond distances in both compounds are typical and require no further comment. The V–C distances average 2.306 (4) and 2.30 (2) Å in **1** and **2**, respectively, and are typical. The V–S distances were found to be 2.424 (1) and 2.430 (1) Å in **1** and average 2.430 (6) Å in **2**. These compare with the V–S distances found in $Cp_2V(SMe)_2$ (2.422 (1) Å)[4] and are slightly shorter than those found in $Cp_2V(SPh)_2$ (2.448 (3), 2.470 (2) Å).[17] These differences are attributable to both the lesser steric demands of the chelating ligands in **1** and **2** and the greater basicity of the alkanedithiolate in comparison to benzenethiolate. The S1–V–S2 angles are 86.91 (4)° and average 79.8 (2)° in **1** and **2**, respectively. These are smaller than that seen in $Cp_2V(SMe)_2$ (88.7 (1)°),[4] which is consistent with the presence of the six- and five-membered chelate rings in **1** and **2**, respectively. The S–V–S′ angle in **1** is also consistent with that predicted on the basis of the minimization of the total Hückel energy as a function of the S–V–S′ angle for the model $Cp_2V(SH)_2$. As expected, the formation of the six-membered ring introduces little, if any, strain at V.

The crystallographic studies of **3** and **4** confirmed that they are dimeric. Compound **3** is the known species $CpV(\mu\text{-}SCH_2CH_2S)_2VCp_2$.[14] A full structural description has been published by Rajan et al.[20] The structurally similar compound **4** also contains two vanadium centers, each of which are π-bonded to a cyclopentadienyl ring, as well as four sulfur atoms that bridge the two metal centers (Figure 5). The V–S distances in **4** average 2.448 (3) Å, which is slightly longer that of 2.425 (1) Å seen in **3**. The V–V′ distance of 2.520 (2) Å is similar to the V–V′ distance of 2.542 (1) Å seen in **3** and is consistent with the presence of a formal metal–metal bond.

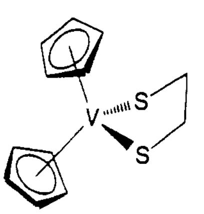
The crystallographic symmetry requires that the dimeric molecule **5** sits on a 2-fold axis of symmetry, and thus only half of the molecule constitutes the asymmetric unit. Two π-bonded cyclopentadienyl rings and a sulfur atom comprise the pseudotrigonal coordination sphere of the vanadium (Figure 6). The V–C distances in **5** average 2.27 (2) Å, while the V–S distance is 2.426 (5) Å, both of which are similar to those seen in **1**. The geometry about V is best described as a pseudotrigonal plane, considering the S and the two centroids of the cyclopentadienyl rings. The sum of the angles about V in this trigonal plane is 349.9°. Steric interactions between the C1–C5 cyclopentadienyl ring and the phenyl ring of the ligand presumably account for the slight displacement of S1 toward the C6–C10 cyclopentadienyl ring. This view is substantiated by the close approach of C11 to H3 (2.621 Å) and of H1 to H12 (2.648 Å).

Mechanistic Considerations. The characterization of **1**–**6** offers some implications regarding the reaction pathways accessible via such oxidative additions reactions. The initial reaction between Cp_2V and a dithiol is undoubtedly oxidative addition of S–H to give the transient thiolate–hydride V(IV) species A. Intramolecular loss of H_2 from such an intermediate results in chelate ring closure and yields V(IV) products such as **1** and **2**. This mechanism is consistent both with the observed V product and with the evolution of H_2 during the reaction.

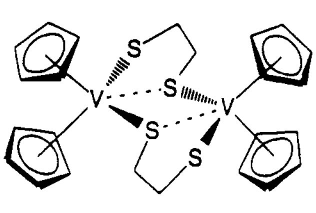


A

In the case of **3**, the mechanism of formation is not clear. It is reasonable to suggest that oxidative addition of ethanedithiolate to Cp_2V yields the initial product $Cp_2V(SCH_2CH_2S)$ (B).



B



C

Extended Hückel calculations have shown that the optimum S–V–S angle for the model compound $Cp_2V(SH)_2$ is 88.7°.[3] Thus, a significantly smaller bite angle, as is observed in **2** and expected for B, is destabilizing. In the case of B, it may be that the lesser steric demands of the chelate compared to that in **2**, contribute to reactivity by permitting dimerization, yielding the V(IV) intermediate C, similar in structure to the known Ti and Zr species.[8–10] Such dimerization requires nucleophilic attack of the SOMO of the $Cp_2V(SR)_2$ moieties, a reaction pathway which has been previously postulated in several reactions of vanadocene derivatives.[21] Subsequent loss of $C_{10}H_{10}$ from this dimeric intermediate would afford the V(III) dimer **3**.

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(21) Kowaleski, R. M.; Basolo, F.; Osborne, J. H.; Trogler, W. C. *Organometallics* **1988**, *7*, 1425 and references therein.

It is interesting that the analogous 1,2-benzenedithiolate dimer **4** is accessible from $CpV(CO)_4$. Presumably, the presence of only one cyclopentadienyl ring and the lability of the CO ligands facilitate dimerization. This may occur via oxidative addition of dithiol to V(I), affording a coordinatively unsaturated V(III) species, which then dimerizes as a result of the basicity of the thiolate ligands. In the case of 1,3-benzenedithiolate, chelation is precluded, resulting in the formation of **5**. Although not confirmed, it is suggested that the formation of the V(III) species **5** occurs via intermolecular loss of H_2 from an intermediate hydride analogous to A. In a similar sense, steric factors have been previously shown to favor V(III), as the reaction of Cp_2V with PhSSPh yields $Cp_2V(SPh)_2$,[17] while the analogous reaction with $Cp^*{}_2V$ affords $Cp^*{}_2VSPh$[18] and the reaction of Cp_2V and HS-$(C_6H_2(t\text{-}Bu)_3)$ gives $Cp_2V(S(C_6H_2(t\text{-}Bu)_3))$.[19]

Summary

Facile synthetic routes to monocyclopentadienyl– and dicyclopentadienyl–vanadium dithiolate derivatives have been developed on the basis of simple oxidative addition reactions. The products from these seemingly similar reactions, reveal an interesting diversity of both structure and oxidation state. Herein, mono- and bimetallic V(IV) species and two types of bimetallic V(III) species, as well as electrochemical evidence for mononuclear V(V) dithiolate derivatives, have been observed. Mechanistic considerations offer some insight into the reaction pathways that are possible and confirm that the course of these reactions is subtlely dependent on both electronic and steric factors.

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Supplementary Material Available: Tables of crystallographic data thermal parameters, and hydrogen atom parameters (9 pages). Ordering information is given on any current masthead page.